LA-UR-03-4363

RTG Mixed Waste Evaluation

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For the

Los Alamos National Laboratory
Off-Site Source Recovery Project

Reviewed/Approved____________________ **Date** 7 / 24 / 03

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Los Alamos National Laboratory
Analytical Chemistry Sciences

CERTIFICATE OF ANALYSIS

Customer: Don L. Quintana

SDG: 00121302

00121302-001MS

Matrix Spike

QC ID	Analyte	Flag	Result	Units	Spike Amount	%R:
SW846_6010W	Silver		0.560	mg/L	0.555	97
SW846_6010W	Arsenic		0.09	mg/L	0.111	80
SW846_6010W	Barium		1.50	mg/L	0.555	94
SW846_6010W	Cadmium		0.560	mg/L	0.555	101
SW846_6010W	Chromium		0.590	mg/L	0.555	101
SW846_6010W	Lead		1.50	mg/L	0.555	85

LCS

QC ID	Analyte	Flag	Result	Units	QC Value	%R:
00.43371-AES	Silver		0.045			90
00.43371-AES	Arsenic	H	0.053			133
00.43371-AES	Barium		0.32			107
00.43371-AES	Cadmium		0.03			100
00.43371-AES	Chromium		0.49			98
00.43371-AES	Lead		0.3			100
00.43371-AES	Selenium	H	0.12			120

Method Blank

QC ID	Analyte	Flag	Result	MDL	Units
3015-AES-BLK	Silver	<	0.002	0.002	mg/L
3015-AES-BLK	Arsenic	<	0.03	0.03	mg/L
3015-AES-BLK	Barium	<	0.001	0.001	mg/L
3015-AES-BLK	Cadmium		0.002	0.002	mg/L
3015-AES-BLK	Chromium		0.003	0.003	mg/L
3015-AES-BLK	Lead		0.02	0.02	mg/L
3015-AES-BLK	Selenium		0.06	0.06	mg/L

RTG Mixed Waste Evaluation

Introduction

Because of the presence of lead telluride in thermocouples in the thermal-electric systems and silver in solder used for electronic circuitry, many RTGs could potentially be classified as mixed waste. Classification of RTGs as mixed waste can directly and adversely impact storage of these devices at selected DOE sites due to existing RCRA permit restrictions prohibiting import of hazardous materials. This issue was therefore assessed to determine if RTGs were mixed waste as defined by EPA using the TCLP testing procedures.

Approach

A SNAP-21B model RTG was selected to conservatively represent an upper bound on the predicted lead and silver concentrations for all RTGs. The SNAP-21B was selected because the quantity of lead and relatively low total weight of 516 pounds yielded a relatively large lead-to-total weight (Pb/wt) for the RTG. Most other RTG models weigh in excess of 1500-3000 pounds, which would yield even smaller lead-to-total weight ratios and, correspondingly, lower theoretical concentrations of lead and silver. Theoretically maximum leachate concentrations were first calculated for lead and silver following the prescribed TCLP formula per EPA Method 1311. Using this approach, the total lead quantity reported by Meyer (1998) for the SNAP-21B is 328 grams or 0.14 % of the total RTG weight. The theoretical concentration was conservatively estimated to result in a leachate concentration of 70 ppm, which is above the TCLP limit of 5 ppm.

A detailed assessment of silver mass present in the SNAP-21B RTG was conducted which estimated that 14.5 grams of silver is present as silver welds and silver leads (Rellergert, 2001). This detailed estimate of silver results in a conservative leachate concentration of 3.1 ppm, which is below the TCLP limit of 5 ppm. Silver was therefore not considered to be a potential TCLP constituent in RTGs. Because lead was calculated to exceed the established TCLP limit, TCLP tests were conducted to ascertain actual concentrations of leachable lead. Chromium and all other TCLP constituents were also analyzed in leachate solutions. It should be noted that according to an 8/18/92/ Federal Register (57CFR37237), EPA does not consider discarded stainless steel artifacts to be hazardous waste (Rellergert, 2001).

The TCLP results for the SNAP-21B RTG were then use to extrapolate to other RTGs. The TCLP results, in combination with the Pb/wt ratios for other RTGs, to determine the Pb concentrations that would be expected if a TCLP test was conducted for another RTG. For the other RTGs, the quantity of lead in the different models was estimated from the power output of the RTG on the basis that the thermal generator efficiencies would not differ from the SNAP-21B by a factor greater than 2 to 3. Then the lead-to-weight ratios

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Customer: Don L. Quintana

SDG: 00121302

INORG-ICPES

SW846_6010W, Trace Metals, ICPOES Liquid

Customer ID: Sample #1 Collection Date: 12/11/00 Matrix: Misc. Materials, Solids Sample ID: 00121302-001

Analyte	Flag	Result	Uncertainty	MDL	Units	Analysis Date
Ag		0.024	0.003	0.003	mg/L	12/15/00
As	<	0.04		0.04	mg/L	12/15/00
Ba		0.976	0.098	0.001	mg/L	12/15/00
Cd	<	0.003		0.003	mg/L	12/15/00
Cr		0.030	0.005	0.005	mg/L	12/15/00
Pb		1.03	0.10	0.03	mg/L	12/15/00
Se	<	0.03		0.03	mg/L	12/15/00

Customer ID: Sample #2 Collection Date: 12/11/00 Matrix: Misc. Materials, Solids Sample ID: 00121302-002

Analyte	Flag	Result	Uncertainty	MDL	Units	Analysis Date
Ag		0.050	0.005	0.003	mg/L	12/15/00
As		0.06	0.04	0.04	mg/L	12/15/00
Ba		0.908	0.091	0.001	mg/L	12/15/00
Cd	<	0.003		0.003	mg/L	12/15/00
Cr		0.025	0.005	0.005	mg/L	12/15/00
Pb		0.35	0.03	0.03	mg/L	12/15/00
Se	<	0.03		0.03	mg/L	12/15/00

QUALITY ASSURANCE REPORT

for INORG-ICPES

00121302-001D **Duplicate**

QC ID	Analyte	Flag	Result	MDL	Units	Sample Result	RPD:
SW846_6010W	Silver		0.027	0.003			11
SW846_6010W	Arsenic	*	0.04	0.04			179
SW846_6010W	Barium		1.03	0.001			5
SW846_6010W	Cadmium	*	0.003	0.003			181
SW846_6010W	Chromium		0.03	0.005			
SW846_6010W	Lead		1.11	0.03			8
SW846_6010W	Selenium		0.03	0.03			8

Page 2 of 3

were determined from published data on the total weight of the RTGs. The lead-to-weight ratios were compared to the SNAP-21B to determine if the projected leachate Pb concentrations would exceed the allowable Pb concentration of 5 ppm. As a check on the reasonableness of this approach, published data for the SNAP-7E and TRACS-25A RTGs were used to compare the projected lead-to-weight ratios with the actual.

SNAP-21B TCLP Test Results

The composition of the SNAP-21B RTG as reported by Meyer (1998) is given in Table 1.

Table 1. SNAP-21B Materials Composition

Material	Mass of Material, (lbs)	% of Total Mass
Pb-Te	1.224	0.25
Hastolloy C	4.0	0.83
Depleted Uranium	242.0	50.2
Inconel X750	1.6	0.33
Stainless Steel 316	58.8	12.2
Titanium	151.0	31.3
Iron	3.2	0.66
Copper	24.4	5.06
Aluminum	1.6	0.33

Two 105 gram representative samples were prepared using the above composition. Materials such as strontium titianate were eliminated if their percentage composition was less then a few percent of the total weight. The small percentages of Hastaloy C and Inconel X750, which are high-nickel alloys, were added to the stainless steel fraction. Organic compounds were also eliminated from the composition. The sample composition is shown in Table 2

Table 2. SNAP-21B Sample Composition

Material	**% of Total**	**Grams in Sample**
Pb-Te	0.25	0.267*
Depleted Uranium	50.2	52.693
Stainless Steel 316	12.2	12.803
Titanium	31.3	32.879
Iron	0.66	0.697
Copper	5.06	5.313
Aluminum	0.33	0.348

*Because half of the P-legs in the SNAP21B also contain a small fraction of tin, the quantity of Pb-Te added to the sample was adjusted to 243 mg instead of the 267 mg to maintain the lead at the same percentage of the total mass.

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-- CERTIFICATE OF ANALYSIS --

Sample Delivery Group:
00121302

Customer:

Don L. Quintana
ESA-EPE / J576
LOS ALAMOS, NM
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Explanation of Flags:
< - Result is less than MDL
H - Result is above upper limit
L - Result is below lower limit

Team Leader ______________ Date 12/22/00

QA Officer Peter C. Lindell ______________ Date 1/2/2001

GUIDANCE FOR THE "PROPER" USE OF C-ACS CERTIFICATES OF ANALYSIS

As guidance for the proper use of this Certificate of Analysis, it should be emphasized that the Los Alamos National Laboratory, Chemistry (C) Division, Analytical Chemistry Sciences (ACS) Group is concerned with fostering excellence in the analyses reported. Therefore, if this Certificate of Analysis is to be quoted, it is recommended that results along with the associated Case Narrative be quoted in their entirety, as excerpts out of context can be misleading.

Friday, December 22, 2000

Each of the above sample materials were cut into pieces to pass a one-cm sieve, consolidated, and subjected to a TCLP leach test using acetic acid under prescribed EPA test conditions. One sample was prepared with a mass of 243 mg of lead telluride in powder form obtained from a specialty alloy supplier. The second sample was prepared from solid N-leg thermocouple material. The required mass of lead was determined based on a percentage weight of 0.14% for the SNAP-21B RTG. Lead in the powder and the solid material was present as 62% of total weight of lead telluride. Tests were conducted at LANL's analytical laboratory, which is approved to perform SW846 analyses by the state of New Mexico.

Results for the representative samples were 1.0 and 0.35 ppm for the samples containing powdered and solid lead telluride, respectively. The chemistry results report is given in Appendix A. A larger concentration was expected for the powdered material due to increased surface area available for reaction with the acetic acid. Both results were well below the limit of 5 ppm. Based on the conservative assumptions used to determine the mass of lead in samples and the rigorous testing conditions conducted for 18 hours, it can be concluded that lead is not a RCRA constituent in the SNAP-21B. All other TCLP constituents, including As, Ba, Cd, Cr, and Se were also well below leachate concentration limits. Chromium concentrations were 0.03 and 0.025 ppm for the powdered and solid samples, respectively. Based on the TCLP analytical results, it is concluded that the SNAP-21B RTG is not mixed waste.

Extrapolation to Other RTGs

A SNAP-21B RTG contains 328 g of lead in 24 lead telluride (PbTe) thermocouples (Meyer, 1998). The total weight of a SNAP-21 is 234.5 kg. The Pb/wt ratio for a SNAP-21B is therefore 0.14%. The Toxicity Characteristic Leaching Procedure (TCLP) leach tests resulted in leachate concentrations of 1.0 and 0.35 ppm for samples containing powdered and solid PbTe, respectively. Since these results are well below the TCLP hazardous waste limit of 5.0 ppm for lead, and lead was the only hazardous material in the SNAP-21B identified as potentially exceeding TCLP limits, the SNAP-21B is not mixed waste. Moreover, based on these results, it can also be said that any RTG with a Pb/wt ratio less than 2% (5 ppm/0.35 ppm x 0.14%) would also be non-hazardous for lead.

Estimated Pb/Wt Ratios for Other RTGs

An estimate of Pb/wt ratios for other RTGs has been developed using the assumption that the weight of lead in the thermocouple is proportional to the thermal output of the RTGs. This is a reasonable assumption for this preliminary determination based on the range of thermal generator efficiencies for the RTGs. Differences in the thermal efficiencies that would affect the Pb content of the RTGs are not likely to vary greater than a factor of 2 to 3. The data on the curie content and RTG weights as shown in Table 3 has been extracted from Moose (1981).

QC Summary

Reagent Blank
ICP-AES: Results were below our detection limits for all analytes.

Laboratory Control Samples (LCS):
ICP-AES: Recovery within 20% of expected for all analytes except As (Se is at 120% recovery). The As LCS is at the detection limit for ICP-AES (it is designed for GFAA analysis). The As recovery in the LCS is high, but the matrix spike and calibration verification samples indicate that 1\S is not biased in this analysis.

Duplicate:
ICP-AES: RPD of +/- 20% for all analytes present above the detection limits. There was some variability in the lead value between sample # 1 and sample #2; see discussion above.

Matrix Spike:
ICP-AES: Recovery within 20% of expected for all analytes.

Runtime QCs:
ICP-AES: Initial and continuing calibration verification standards were all within 10% of expected values except for Se. The Se CCVs were high; however, as all sample results were below detection limit, no bias is observed in your sample results. As is high on the final CCV; again, as your samples are at or below detection limit, no bias is observed. Blank checks were all below detection limits. Interference check standard was within 15% of expected value for all analytes.

The thermal output of the SNAP-21 is 210 watts and it has 328 gms of Pb. Using these assumptions, the following Pb/wt ratios were obtained:

Table 3. Estimated Lead Content of Other RTGs

RTG	Curie Content, kCi	Watts-th.	Pb Mass, g	Total Weight, kg	Pb/wt %	Factor Below Limit
Sentry	17.5	117	185	764	0.0243	82.5
SNAP-7C	40	269	423	836	0.051	39
SNAP-7A	40.8	274	432	850	0.051	39
SNAP-7B	225	1510	2381	2091	0.114	18
SNAP-7D	224	1503	2370	2091	0.113	18
SNAP-7E	31	208	328	2727	0.012	166
SNAP-7F	212	1423	2244	2091	0.11	19
URIPS-PI	6.6	44	70	380	0.018	109
URIPS (Gulf)	9	53.7	85	382	0.022	90.2
URIPS-8	55	369.1	582	800	0.0728	27.5
Sentinel-3	25	168	265	1227	0.022	93
MW-3000	20	134	212	1273	0.017	120
Millitracs	25	170	265	159	0.17	12
Sentinel-25A	125	839	1323	1364	0.097	21
Sentinel-25CI	109	732	1154	909	0.127	16
Sentinel-25D	106	711	1122	1364	0.082	24
Sentinel-25E	106	711	1122	1895	0.059	34
Sentinel-25B	106	711	1122	1500	0.075	27
TRACS-25	118	792	1249	668	0.187	11
Sentinel-8	37	248	392	1432	0.027	73
SNAP-23	166	1114	1757	545	0.322	6
Sentinel-8	45	302	476	1432	0.033	60
SNAP-21	32	215	339	645	0.116	17
Sentinel-25F	108	725	1143	636	0.18	11
Sentinel-100F	328	2201	3471	1236	0.281	7

Based on these assumptions, the Pb/wt ratios for all of the RTG models are below the allowable Pb/wt ratio of 2% by factors ranging from 6 to 166. Only the SNAP-23 and the Sentinel-100F RTGs are within an order of magnitude of the allowable limit. The estimated Pb contents presented for these two RTGs indicate that even if the actual Pb content of the RTGs is different from that estimated by the above method, the difference must be larger than a factor of 6 before the allowable limit of 2% is reached. This does not seem likely. However, as a check on the reasonableness of this method, physical data on the Pb content and total weight were available on the SNAP-7E and TRACS-25A RTGs.

The data used to calculate Pb/wt ratios were taken from Table 1, "Performance Characteristics of the SNAP-7E and TRACS-25A Generators," Appendix F, "Safety

Los Alamos
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Memorandum

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To/MS Don Quintana, ESA-EPE, MS J576
From/MS: Eva R. Birnbaum, C-ACS, MS E518
Phone/FAX: 667-7538/665-6561
Symbol:
Date: 12/22/00

Case Narrative for Sample Delivery Group 00121302

Sample #1 and Sample #2 were received at TA-50 on 12/13/00. These samples were composite samples generated by ESA-EPE. At TA-50, we added uranium turnings to sample #1, and uranium pellets (with a small amount of turnings) to sample #2, in amounts specified by Don Quintana. No size reduction was performed as all pieces were already small enough to pass through a 1-cm sieve. The total sample weights were 105.04 g for sample #1 and 104.68 g for sample #2. No representative sub-sample could be taken for the pH test, so extraction fluid #1 was used for the TCLP extraction. This extraction fluid was chosen because that is the fluid that has been used for the majority of samples here at TA-50. Also, it is expected that had the pH pre-test been performed, fluid #1 would have been indicated (the pH of the sample is anticipated to have been < 5 after the addition of 1.0 N HC1).

The TCLP extraction (SW 846 method 1311) was begun on 12/13/00. The extracts were digested by SW 846 method 3015 on 12/14/00. ICP-AES (SW 846 method 6010B) analysis was performed on 12/15/00.

The results are below RCRA levels for all analytes. This indicates that the lead telluride did not leach into the extraction fluid. If all of the lead telluride had dissolved, the anticipated concentration in the extraction fluid would have been approximately 75 ppm (0.36 mM). Instead, we found 1 ppm lead in sample #1, and 0.35 ppm in sample #2.

The dissolution is not limited by acetate. Lead acetate is highly soluble in water, and the extraction fluid has a concentration of 0.09918 M in acetate. Total consumption of the acetate would have resulted in a 0.04959 M solution of $Pb(OAc)_2$, allowing dissolution of up to 10,300 ppm of lead. Obviously, there was not this much total lead in the sample.

There are several possible reasons why the PbTe did not dissolve; thermodynamic and kinetic. If PbTe has a high lattice energy, it is thermodynamically more stable in the solid form. As lead is added to Te to reduce corrosion, it is likely that this alloy is very stable. Heat or some other form of energy (greater than the tumbling of a TCLP extraction) would be required to overcome the barrier to dissolution. Alternatively, there could be a kinetic barrier, and the conversion of PbTe to ions is a slow process that does not proceed significantly in the 18 hours of the TCLP extraction.

Please contact me if you wish to discuss any of these issues further.

Hazard Analysis for SNAP-7E and TRACS-25A Radioisotope Thermoelectric Generators," HNF-SD-ISB-007, Revision 1, April 22, 1991 as shown below in Table 4.

Table 4. Lead Content of the SNAP-7E and TRACS-25A RTGs

RTG	Total Pb, g	Total Wt., kg	Pb/Wt %
SNAP-7E	950	2191	0.043
TRACS-25A	520	668	0.078

The lead content of the SNAP-7E as given in the Safety Hazard Analysis is 950 g as compared to the content of 328 g from the above method. The actual content is a factor of 2.9 larger than the content from the estimate. This is likely due to the lower generator efficiencies achieved in the earlier RTG designs. The actual lead content of the TRACS-25A is given as 520 g as compared to 1249 g from the above estimate. This is a factor of 2.4 less than the content from the estimate. This lends supports to the conclusion that the actual Pb content is not likely to differ from the estimated content any greater than a factor of 2 to 3.

Based on these data and analysis, these RTG models are non-hazardous for lead and, since they contain no other potentially hazardous materials (Carson, 2000), are not mixed. Accordingly, it is concluded that all of the RTGs listed above are classified as non-hazardous.

References

1. Rellergert, Carla. Chemical Characterization on DR 994333. Sandia National laboratory. February 12, 2001.

2. Carson, Susan, 2000. "RTG Notes and Questions," Sandia National Laboratories, Albuquerque, New Mexico, November 2000.

3. Meyer, Dann, 1998. "SNAP-21: Results of Investigation of Potential Hazardous Waste," Sandia National Laboratories, Albuquerque, New Mexico, April 22, 1998.

4. Teledyne Energy Systems, 1991. "Resubmittal of Prior Applications and Supplements for Approval to Transport the Sentinel (LCG) - 25A Radioisotope Thermoelectric Generator as a Type B ( ) Package," Revision 2, TES-3206, Teledyne Energy Systems, Timonium, Maryland, December 1991.

5. United States Nuclear Regulatory Commission (NRC), 2000. "Safety Evaluation Report, Docket No. 71-5862, Model No. Sentinel-100F Package, Certificate of Compliance No. 5862, Revision No. 8," U.S. Nuclear Regulatory Commission, Washington, D.C., October 6, 2000.

6. Moose, J.M., 1981. "Thermoelectric Generation Handling Study", Rockwell International, Rockwell Hanford Operations, Energy Systems Group, Richland Wash., RHO-CD-1241, April 1981.